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Substantive Intumescence from Phosphorylated 1,3-propanediol Derivatives Substituted on to Cellulose

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Synopsis

Cellulose flame retarded with an ammonia-cured, polycondensed tetrakis (hydroxymethyl) phosphonium-urea derivative (as Proban CC®,Rhodia) phosphorylated by cyclic 1,3-propanediol phosphoryl chloride or CPPC and cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride or CDPPC can give phosphorus levels up to 6.9%(w/w). Such high levels suggest up to 35.5% yields of reaction if the free secondary amine groups present in the cross-linked flame retardant and the C (6) primary hydroxyl groups are the assumed phosphorylation sites.

The presence of substituted propanediol phosphonate moieties in the fibres significantly increases char formation above 400^{o}C and scanning electron microscopy indicates that the char has an intumescent structure. The influence of chemical structure of the propanyl moeity to the reaction extent of the possible phosphorylation sites and the char formation mechanism during thermal pyrolysis of the modified samples are discussed.

Keywords: Fibers, Flame retardance, Pyrolysis, Cellulose, Phosphorylation, Proban®, Tetrakis(hydroxyl methyl) phosphonium condensate, Char, Intumescents

1. Introduction

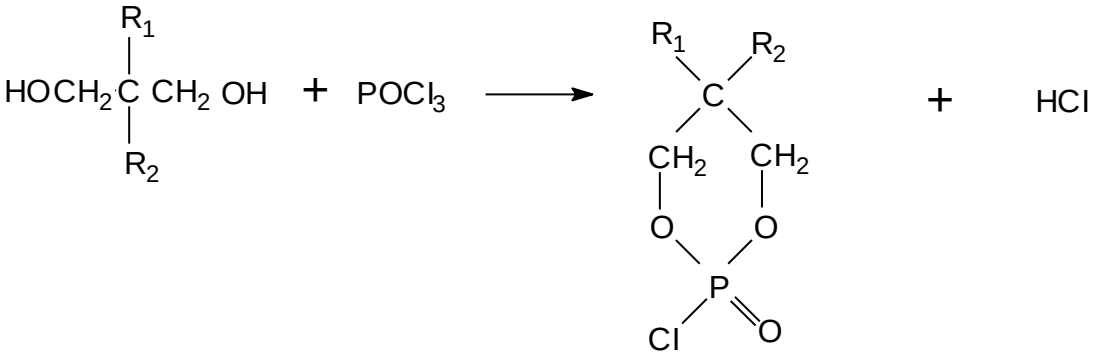
Our previous research [1] has demonstrated that phosphorylation of the anhydroglucopyranose hydroxyl groups in cellulose with spirocyclic pentaerythritol di(phosphoryl chloride) or diphosphochloridate, SPDPC can give rise to phosphorus levels as high as 2.47% and a yield of 22.7% with respect to substitution of one C(6) hydroxyl group per repeat unit by one phosphoryl moiety. Such a level of phosphorus substitution has significantly enhanced the char formation and suggested possible flame retardant activity.

Subsequent work [2] has also demonstrated that phosphorylation of cellulose flame retarded with an ammonia-cured, polycondensed tetrakis(hydroxymethyl) phosphonium-urea derivative with SPDPC can yield phosphorus levels in excess of 10%(w/w). Such high levels suggest up to 93% yields of reaction if phosphorylation of the free secondary amine groups present in the cross-linked flame retardant is the assumed site. The substituted pentaerythritol phosphate moieties significantly increase char formation and give durability to water-boiling, as well as intumescent behaviour in terms of inflated char structure.

More generally, it may be proposed that other polyol phosphoryl chlorides would similarly phosphorylate cellulose and its derivatives to yield potentially intumescent flame retardant behaviour. It is proposed also that the particular success achieved with SPDPC to date is partly a consequence of the stability of the 6-membered cyclophosphate moeities within SPDPC. Thus if we wish to compare the char-forming behaviour of other phosphorylated polyols, it is necessary to retain this structure and yet modify the hydrocarbon moeity and hence carbonaceous char source. With this in

mind, we have selected 1,3 propanediol and its derivatives as possible alternatives to pentaerythritol as the polyol.

Phosphorylation of 1,3-propanediol derivatives can give rise to six-membered ring cyclic propanediol phosphoryl chloride (CPPC) or 2-chloro-2-oxo-1,3,2-dioxaphosphorinane and its derivatives if the following reaction holds true:



where R_1 and R_2 are hydrogen or aliphatic moeties[3]. If $R_1 = R_2 = C_2H_5$, then in a similar manner, 2,2-diethyl-1,3-propanediol phosphoryl chloride (CDPPC) or 2-chloro-5,5-diethyl-2-oxo-1,3,2-dioxaphosphorinane is formed.

It is proposed also that CPPC and its derivatives can also phosphorylate Proban-treated cotton which contains secondary bridge amine groups and possibly unreacted methylol groups. This paper studies the phosphorylation reaction between cyclic 1,3-propanediol phosphoryl chloride (CPPC) and cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride (CDPPC) and Proban-treated cotton and the resulting intumescent char-forming behaviour.

2. Experimental

2.1. Materials

A commercially finished Proban CC (Rhodia)-treated cotton fabric (area density, 166g/m^2) was selected having a level of flame retardancy commensurate with a pass to a typical vertical strip test method such as BS 5438:1989:Test 2. Proban CC is a complex polyphosphine oxide formed within the microfibrillar voids of the celluose structure of the fibre. It is based on an ammonia-cross-linked polycondensate of tetrakis (hydroxymethylol) phosphonium chloride (THPC) and urea [2].

The reagents dimethylformamide (DMF), pyridine, sodium hydroxide were of normal laboratory reagent purity.

2.2. The preparation of CPPC

CPPC was synthesised according to the procedure similar to SPDPC described previously [1]. 15.3g $POCl_3$ was added drop by drop with a separation tunnel to the three-neck flask which contained 7.6g 1,3-propandiol over a period of 20min, the reaction was protected by nitrogen and stirred by a magnetic stirrer. The evolution of gas could be seen soon after the addition of the $POCl_3$. The released HCl gas was absorbed by passing into sodium hydroxide solution. The flask contents were heated to 40ºC slowly in an ethylene glycol bath, and held at 40ºC for an hour. The product is a transparent liquid.

The expected almost 100% quantitative yield [3] was demonstrated by IR analysis which indicated that there was no free -OH group absorption in the region 3590~3650cm^{-1}.

2.3. The preparation of CDPPC

2,2-diethyl-1,3-propandiol, was crushed into a fine powder in a mortar, and 13.2g was transferred into a three-necked flask, under an atmosphere of nitrogen and stirred by a mechanical stirrer. 15.4g $POCl_3$ was added to the flask drop by drop. Bubbles of HCl were seen at 55^0C, and were released very slowly. The flask contents were heated to 90^0C for 10h. The fine white powder of 2,2-diethyl-propandiol soon dissolved, and the reactants became a transparent liquid after the addition of $POCl_3$.

The final product is a viscous liquid, which after 7 days transformed to a white solid cake. Given the anticipated stoichiometric reaction [3], no attempt to purify the crude CDPPC was undertaken. However, the expected quantitative yield was demonstrated by IR analysis which showed absence of free -OH group absorption around 3590~3650cm^{-1}. GC/MS (R=1000) analysis has also shown that the main peak is at mass-to-charge ratio (m/e) of 213, which means that CDPPC (M=212) is the main product.

2.4. Phosphorylation of cellulose and Proban-treated cellulose

Reactions were undertaken according to the same procedure as described before for SPDPC phosphorylation of cellulose and its Proban-treated derivative [1,2].

2.5. TGA analysis:

The TGA curves were obtained by using a Stanton Redcroft TGA 760 instrument under static air with a heating rate of 20^0C/min. About 2.8mg samples were used in each case.

2.6. Optical microscopic and SEM analysis:

For SEM examination, char samples were prepared at 400^0C for 5min in a laboratory furnace in air. Charred samples did not need gold sputter coating, since they produced good quality images because of their inherent conductivity. All the experiments were undertaken at 10.0kV using a Stereoscan 200, TL2025-OM (Cambridge Instruments Ltd)

2.7. The determination of phosphorus content:

Phosphorus analysis of reacted samples was carried out by the molybdovanadophosphoric acid method [4].

2.8. Flammability testing:

Limiting oxygen index (LOI) values were determined on selected larger phosphorylated samples using a standard procedure [5].

3. Results and Discussion

3.1 The degree of phosphorylation

Based on our earlier work [1,2] and by noting the degree of enhanced char formation, reaction of CPPC and/or CDPPC with Proban-treated cotton was undertaken at 160^{o}C for period up to 0-2h at respective ratios of 2:1 and 4:1. These correspond to approximately CPPC:Proban cotton molar ratios of about 2:1 and 4:1 and for CDPPD, 1.5:1 and 3:1 respectively (see below).

Levels of phosphorus, including that for the unreacted Proban-treated cotton of 3.96%, are shown in Table1. For selected CPPC- and CDPPC-reacted Proban-cotton samples, phosphorus analyses after boiling in detergent (1%) solution for half an hour are included in order to ascertain the durability of their phosphorylated analogues to potential laundering.

In order to express these experimental phosphorus levels as yields, the maximum expected theoretical value of phosphorus content can be calculated in a similar manner to that described previously [2]. Given that 100g Proban-treated cotton containing 3.96g phosphorus, also contains 6g water as adsorbed moisture regain, then based on its formalised structure, it contains 3.96(309/62) = 19.7g Proban polymer and 74.3g cellulose, where the repeat unit of the Proban polymer is assumed to have the empirical formula $C_8H_{17}O_4N_5P_2$, M_{pr} = 309 [2].

Assuming that phosphorylation occurs at the bridging secondary amine group in the Proban polymer and the primary hydroxyl group in C(6) in the cellulose ring, after reaction, 1 molecule of CPPC may substitute the active hydrogen present in Proban polymer and the molecular weight of the reacted repeat unit of Proban polymer is:

$$M_{prc} = (309-1)+(156.5-35.5) = 429$$

However, one molecule of CPPC may also substitute the active hydrogen present in the cellulose C(6)-OH and the molecular weight of the reacted repeat unit of cellulose is:

$$M_{cellc} = (162-1)+(156.5-35.5) = 282$$

So the total maximum mass of a phosphorylated 100g Proban-treated cotton sample comprising 19.7g Proban polymer is:

$$6+(19.7/309)* M_{prc} +74.3(M_{cellc} /162) = 162.7g,$$

Within this, the mass of phosphorus is: 19.7(429/309)(31x3/429) + 74.3(31/162) = 20.13g, corresponding to the maximum phosphorus percentage present, as a consequence of CPPC substitution, namely 100(20.13/162.7) = 12.3%. Thus the increase due to substituted CPPC, $\Delta P\%$ = (12.3-3.96)% = 8.34%, where 3.96% is the phosphorus level within the original Proban polymer (see Table 1).

Similarly, for CDPPC reacted samples, M_{cellcd} = (162-1)+(212.5-35.5) = 338, the total maximum mass of a phosphorylated 100g Proban-treated cotton sample comprising 19.7g Proban polymer is 188.4g, in which the mass of phosphorus is 20.13g. This latter is equivalent to a maximum mass of phosphorus percentage present of 10.7%, of which the increase due to substituted CDPPC is 6.74%.

From Table 1, the highest yield achieved for a CPPC-reacted sample is (6.92-3.96)/8.34=35.5%, and for CDPPC, similarly, 39.9%.

While lower yields are achieved than with SPDPC, it is seen that the Proban-treated cotton sample can be more easily phosphoralyted by CPPC (Table 1 and Figure 1) than by CDPPC at 160^0C for reaction times upto 2h [2]. This is probably because of the small molecular size of CPPC relative to CDPPC which has two more ethyl groups. The lower yields relative to SPDPC-reacted samples are difficult to explain because this is considerably larger than the CPPC and CDPPC species. Table 1 also indicates that under the same reaction conditions, the longer the reaction time is, the higher is the phosphorus level. However, while the mass ratio, CPPC/sample, shows the effect on the phosphorus level for ratios above 2, the mass ratio of CPPC/NaOH does affect the phosphorus level, in a proportionate manner. This latter effect is probably because the higher pH value will promote the phosphorylation via removal of released HCl gas.

3.2 Thermal analysis and char enhancement

In the following discussion, all experimental TGA curves are compared with expected curves calculated from weighted fractional TGA responses of CPPC or CDPPC. The method of calculation of composite TGA responses is described in reference 1.

CPPC reacted samples: Figure 2 shows the TGA curve of CPPC reacted Proban-treated cotton at the mass ratio of 2:1:0.5 (CPPC/Proban cotton/NaOH) carried out at 160^0C for 60min. After modification, a significant increase in char formation of about 200% at 800^{o}C compared with the control Proban-cotton can be seen. This enhancement occurs in a region where char oxidation is normally occurring and

previous research shows that enhanced char formation over this temperature region is synonymous with improved fire performance [6,7].

The TGA response of the same reacted sample washed in boiling 1% detergent solution for half an hour is also shown in Fig. 2, and it is seen to be lower than that before washing. However, there is still about 100% char enhancement at 800^{o}C compared with the control sample suggesting that the phosphorylated 1,3-propanediol derivatives are reasonably resistant to boiling in water and hence durable to laundering.

Figure 3 shows the TGA curve of CDPPC reacted Proban-treated cotton at the mass ratio of 2:1:0.5 (CPPC/Proban cotton/NaOH) at 160^{0}C for 60min. Like the CPPC-reacted sample, after phosphorylation, a similar significant increase in char formation at 800^{o}C can be seen. After boiling in boiling 1% detergent solution for half an hour, a reduction in char occurs relative to the unwashed sample, but it is still again higher than that from the control sample. This suggests that the CDPPC phosphorylated Proban treated cotton samples are similarly quite resistant to boiling in water and hence durable to laundering.

Comparing SPDPC, CPPC and CDPPC-reacted sample behaviours, the washed and unwashed SPDPC reacted samples show only a little difference [1,2], while CPPC and CDPPC-reacted samples, show larger differences in char before and after washing. This suggests that SPDPC-reacted samples may be more durable to laundering treatment. This may possibly because of the bi-functionality of SPDPC which may react with the substrate at both ends forming a cross-linked structure having greater resistance to hydrolytic scission.

In order to investigate the effect of reaction time on the char residue, TGA curves of CPPC phosphorylated sample reacted at 30 and 60 min respectively are shown in

Fig. 4. Above 320^{o}C, the two curves are little different, suggesting that most phosphorylation has completed in half an hour; phosphorus concentrations in Table 1 also support this assumption.

Whether the phosphorylation is carried out using CPPC or CDPPC, the sample shows a lower initial degradation temperature (around 220^{o}C, Figures 2, 3 and 4) than the control Proban cotton sample (around 380^{o}C). Based on our previous work, it is supposed that the CPPC and CDPPC-phosphorylated samples in Figures 2, 3 and 4 have the similar degradation mechanisms as the SPDPC-phosphorylated celllulose samples [1].

In order to demonstrate that the fractional increase in char at any temperature above 400^{o}C is dependent upon the level of substituted additional phosphorus present, Fig. 5 shows plots of $(C_s-C_p)/C_p$ (where C_s is the char residue of reacted sample at certain temperature, C_p is the char residue of control sample at certain temperature) versus phosphorus concentration derived from selected CPPC-reacted samples in Table 1. Here it is seen that the fractional char increases with phosphorus content, although enhanced char fractions appear to plateau for 400^{o}C, 500^{o}C and 600^{o}C curves [1,2].

3.3 Char structures: scanning electron microscopy

The microstructure of Proban-finished cotton fibre control sample heated at 500^{o}C for 10min (see Figs 6 (a) and (b)) shows fibrous chars of Proban cotton and CPPC-phosphorylated Proban-finished cotton samples. Compared with the microstructure of Proban-finished cotton control char and, as reported previously for SPDPC-reacted

chars [2], the CPPC-phophorylated fibrous chars have increased diameters. Chars from boiled CPPC-reacted samples in Fig 6 (c) are similar to those in Fig. 6 (b).

Measurement of ten fibre diameters in each of Figs 6 (a) and (b) after averaging gives an unreacted:CPPC-reacted char diameter ratio of 1:1.72. Thus, on average, char diameters produced at 500^{o}C show 72% increase as a consequence of CPPC phosphorylation. This increase will be due partly to the slight char enhancement (see Fig. 5), but in the main is a consequence of voiding and intumescent structure.

Neglecting the slight mass increase, if it is assumed that the CPPC-reacted sample chars are intumescent and that they swell radially only, then their volumes will relate to the square of radial swelling. Therefore, for the chars in Figs 6 (b) and (c) relative to those in Fig. 6 (a), the char volume ratio = $(1.72/1)^2$ = 2.96, ie an increase in volume of 196%. Given that the CPPC-reacted sample corresponds to a phosphorus level of 6.84% (see Table 1), then Fig. 5 shows that indeed the additional char at 500°C is negligible and so the increase in volume of 196% must be due to intumescence. This result compares favourably with SPDPC-reacted sample results in reference [2] which suggested a volume increase of 70% and so have indicated the CPPC-reacted sample is more intumescent than the SPDPC reacted sample at the same phosphorus level.

Figure 7 shows the microstructure of CDPPC-reacted Proban-finished cotton fibre sample heated at 500^{o}C for 10min. It also shows similarly swollen char structures having an unreacted:CDPPC reacted char average diameter ratio of 1:1.68, thereby suggesting a 182 % increase in volume.

3.4 Limiting Oxygen Index Value

The fire performance of selected CPPC/CDPPC-reacted samples was also characterized by LOI measurement. The sample reacted with CPPC at mass ratio of 2:1:0.5 (CPPC/Proban cotton:NaOH) at 160°C for 2h gave a LOI value of 34.2, while that of the CDPPC-reacted sample at the same condition yielded 33.5; both are higher than that of the control sample, which is 32.1. This demonstrates that the phosphorylated 1,3-propanediol derivatives (CPPC and CDPPC) samples are more fire resistant than the parent Proban-treated control sample.

4. Conclusions

These results have shown that like SPDPC, the polyol phosphoryl chlorides CPPC and CDPPC can also phosphorylate active hydrogen atoms present in the secondary amine, cross-linked, THP-urea poly (phosphine oxide) structure (as Proban polymer) within the voidage of cellulosic fibres in high yield, and all phosphorylated samples give intumescent char structures. At short reaction times, CPPC, which has the smallest molecular weight, seems the more active phosphorylating agent with respect to Proban-treated cotton. Strong evidence that the increased chars are intumescent in character have been demonstrated by using SEM for both CPPC and CDPPC-reacted substrates with char volume expansions of up to 182-196% being evident.

Acknowledgements

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Table1 Phosphorus concentrations in CPPC-phosphorylated Proban-treated cotton*

Sample reaction variables	Mass ratio (CPPC or CDPPC/sample/ NaOH)	Time (h)	Temperature (^{0}C)	CPPC		CDPPC	
				P % (w/ w)	P % (w/w, washed)	P % (w/ w)	P % (w/w, washed)
Proban-treated cotton control		0	160	3.96			
Effect of reaction time and mass ratio	2:1:0.5	0.5	160	5.31**	4.69	4.87	3.7
	2:1:0.5	1	160	5.86**	4.58	5.03	4.27
	2:1:0.5	2	160	6.92**	6.13	6.65	4.84
	4:1:1	1	160	5.95	4.95		
	4:1:1	2	160	6.84	6.26		
	4:1:0.5	1	160	4.29**			
	4:1:0.5	2	160	5.01			

*200mg Proban -treated cotton, 5ml DMF

**Indicates samples for which TGA responses are available and char yields are derived in Fig.5

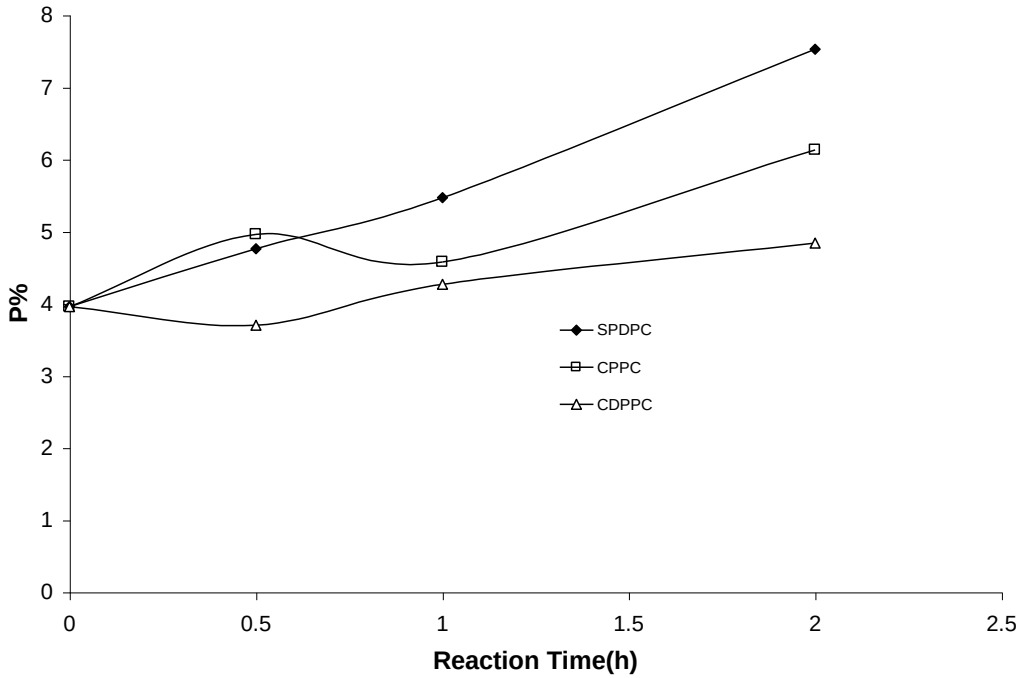


Fig. 1 P% versus reaction time for different polyol phosphoryl chlorides

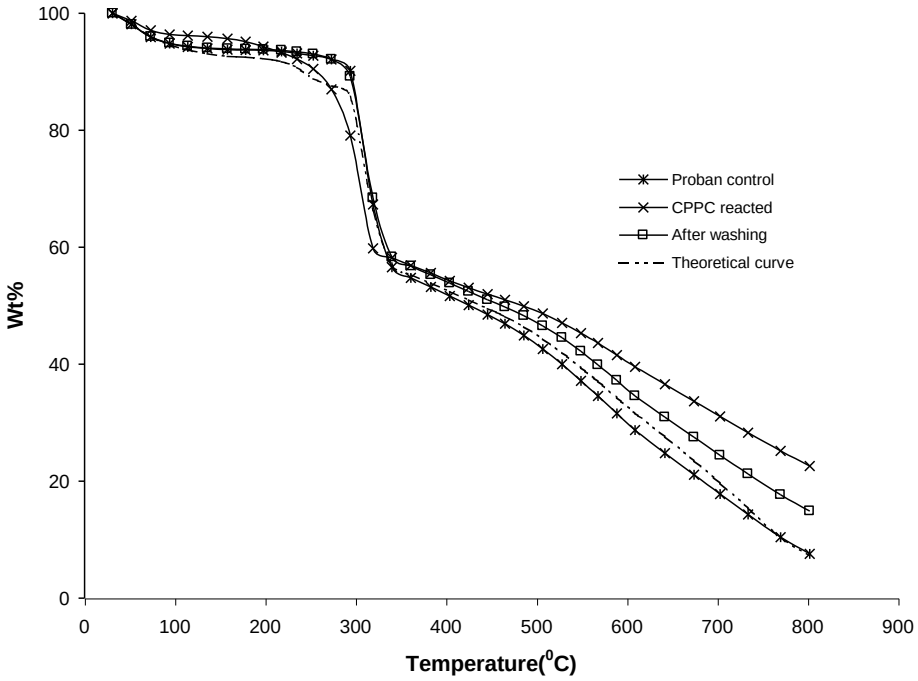


Fig. 2. CPPC-phosphorylated Proban-treated cotton (mass ratio of CPPC/Proban cotton/NaOH = 2:1:0.5) at 160^0C for 60 min

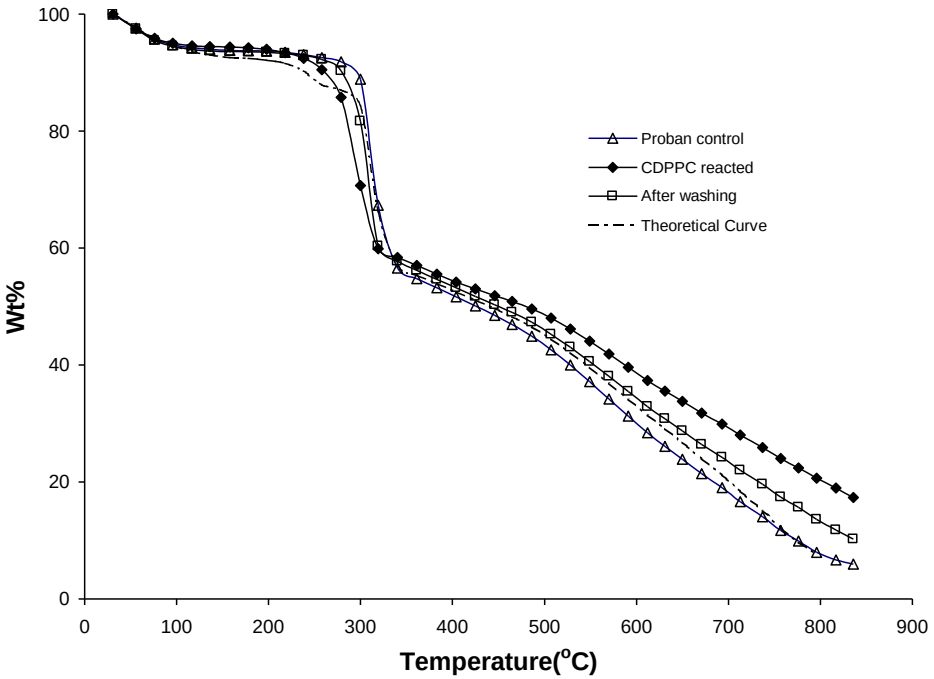


Fig. 3. CDPPC-phosphorylated Proban-treated cotton (mass ratio of CPPC/Proban cotton/NaOH = 2:1:0.5) at 160^0C for 60 min

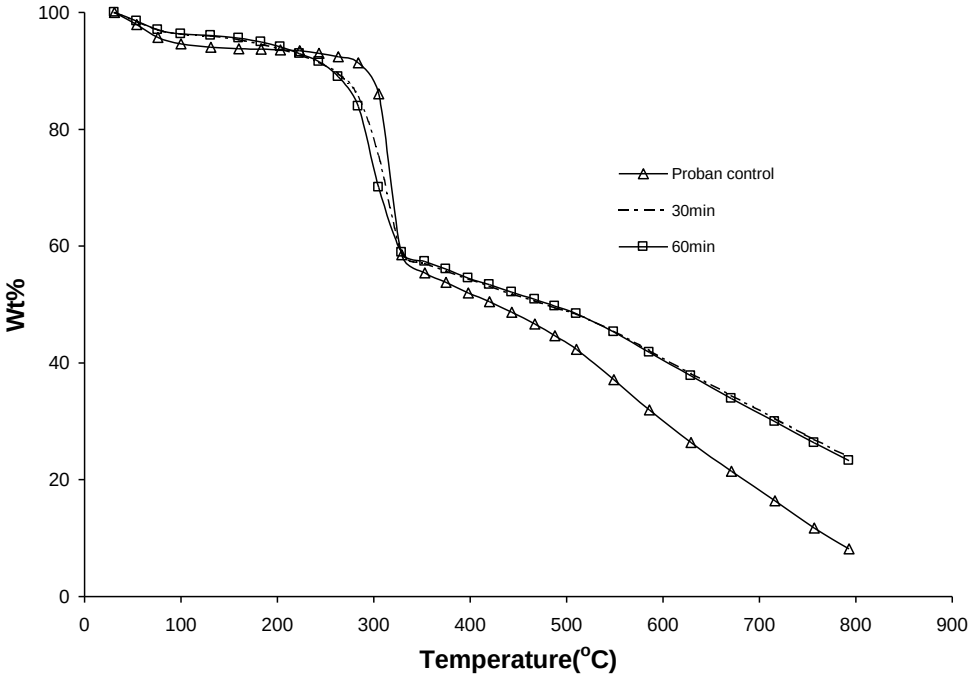


Fig. 4 CPPC-phosphorylated Proban-treated cotton (mass ratio of CPPC/Proban cotton/NaOH = 2:1:0.5) at 160^0C for 30 and 60 min

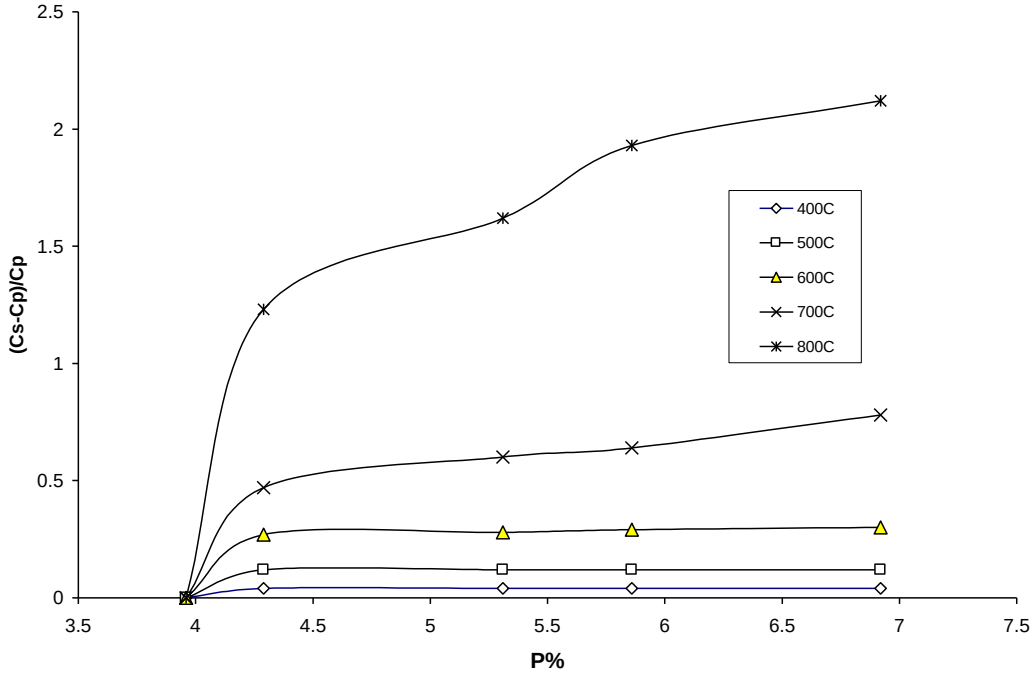
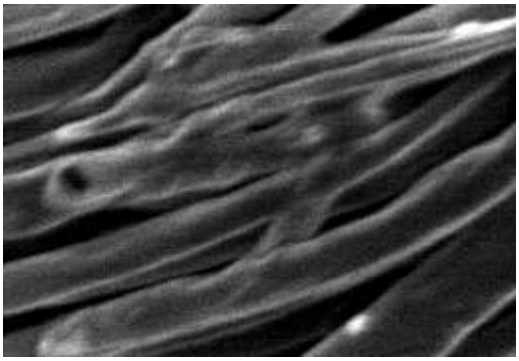
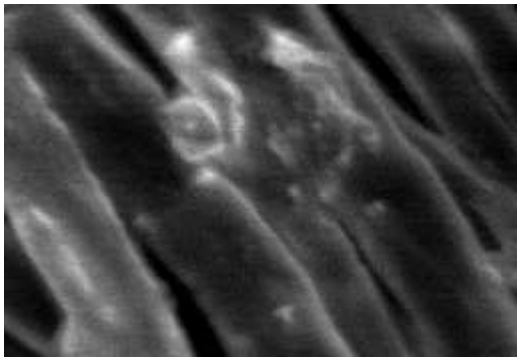


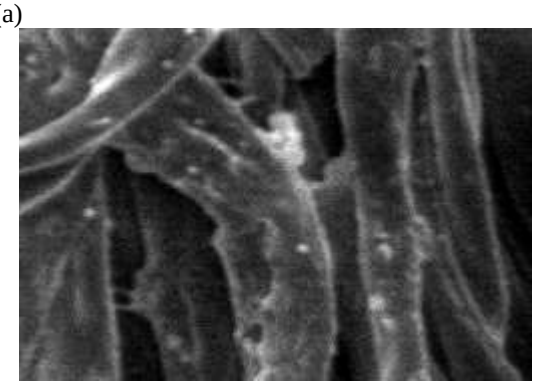
Fig. 5 Plots of $(C_s-C_p)/C_p$ versus P% for all CPPC-treated Proban-treated cottons at designated reaction conditions in Table 1



(a)



(b)



(c)

Fig. 6 (a) Proban control 1500x, heated at 500°C for 10min (b) CPPC-reacted sample chars (120min, CPPC/Proban cotton/NaOH mass ratio = 4:1:1, heated at 500°C for 10min), before washing, 1450x (c) CPPC-reacted boiled sample chars, 1450x

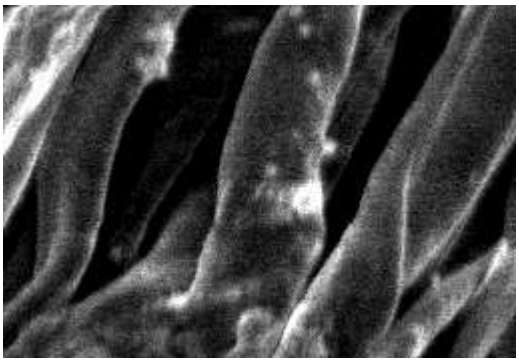


Fig.7 CDPPC-reacted sample chars (120min, CDPPC/Proban cotton/NaOH mass ratio = 2:1:0.5, heated at 500°C for 10min), 1450x,